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(54) **Process for the production of catalysts with improved accessibility**

(57) The present invention is directed to a process for preparing a catalyst comprising combining catalyst components or precursors thereof in an aqueous medium to form a catalyst precursor mixture, feeding the mixture to a shaping apparatus and shaping the mixture to form particles, characterised in that just before the shaping

step the mixture is destabilised. It was found that with this process catalysts can be prepared with both a good attrition resistance and a high accessibility. The invention further relates to catalysts obtainable by this process.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to a process for preparing a catalyst comprising combining catalyst components or precursors thereof in an aqueous medium to form a catalyst precursor mixture, feeding the mixture to a shaping apparatus and shaping the mixture to form particles. The invention furthermore relates to catalysts obtainable by this process.

BACKGROUND OF THE INVENTION

[0002] A common challenge in the design and production of heterogeneous catalysts is to find a good compromise between the effectiveness and/or accessibility of the active sites and the effectiveness of the immobilising matrix in giving the catalyst particles sufficient physical strength, i.e. attrition resistance.

The preparation of attrition resistant catalysts is disclosed in several prior art documents.

[0003] GB 1 315 553 discloses the preparation of an attrition resistant hydrocarbon conversion catalyst comprising a zeolite, a clay and an alumina binder. The catalyst is prepared by first dry mixing the zeolite and the clay, followed by adding an alumina sol. The resulting mixture is then mixed to a plastic consistency, which requires about 20 minutes mixing time. In order to form shaped particles, the plastic consistency is either pelletised or extruded, or it is mixed with water and subsequently spray-dried.

The alumina sol disclosed in this British patent specification comprises aluminium hydroxide and aluminium trichloride in a molar ratio of 4.5 to 7.0.

[0004] This type of alumina sol will be referred to in the present specification as aluminium chlorohydrol.

[0005] US 4,458,023 relates to a similar preparation procedure, which is followed by calcination of the spray-dried particles. During calcination, the aluminium chlorohydrol component is converted into an alumina binder.

[0006] WO 96/09890 discloses a process for the preparation of attrition resistant fluid catalytic cracking catalysts. This process involves the mixing of an aluminium sulphate/silica sol, a clay slurry, a zeolite slurry and an alumina slurry, followed by spray-drying. During this process, an acid or alkaline stable surfactant is added either to the silica sol, the clay slurry, the zeolite slurry, the alumina slurry and/or the spray-drying slurry to prevent gelling or polymerisation of slurry ingredients.

[0007] CN 1247885 also relates to the preparation of a spray-dried cracking catalyst. This preparation uses an aluminium sol, a molecular sieve slurry, clay and an inorganic acid. In this process the aluminium sol is added before the clay and the inorganic acid and the molecular sieve slurry is added after the inorganic acid. It is disclosed that with this preparation process it is possible to change the interactions between the sol particles, thus causing a large fall in viscosity of the slurry, thereby offering the possibility to work with relatively high solids to liquid ratios.

[0008] As already mentioned above, heterogeneous catalysts preferably possess good attrition resistance and high accessibility. In general, as one would expect, the accessibility of the active phase will deteriorate with increasing amounts of binder material. So, the wish for good attrition resistance and high accessibility usually asks for a compromise.

[0009] There is an ongoing need for catalysts which not only possess good attrition resistance, but also possess a high accessibility of the active phase for the compounds to be converted. A process for the preparation of such catalysts is presented in the present specification.

[0010] The present process comprises combining catalyst components or precursors thereof in an aqueous medium to form a catalyst precursor mixture, feeding the mixture to a shaping apparatus and shaping the mixture to form particles, characterised in that just before the shaping step the mixture is destabilised.

The invention further relates to catalysts obtainable by this process.

[0011] More in particular, the process involves feeding suspended catalyst components or precursors thereof from one or more vessels (the 'holding vessels') via a so-called pre-reactor to a shaping apparatus. In this pre-reactor the catalyst precursor mixture is destabilised.

In this specification a destabilised mixture is defined as a mixture whose viscosity is higher after leaving the pre-reactor (and before shaping) than before entering the pre-reactor. The viscosity increase is due to induced polymerisation or gelling of catalyst binder material in the pre-reactor. The viscosity is typically increased from a level of about 1-100 Pa·s at a shear rate of 0.1 s⁻¹ before entering the pre-reactor, to a level of about 50-1000 Pa·s or higher at a shear rate of 0.1 s⁻¹ after leaving the pre-reactor. In any case, it is preferred to induce a viscosity increase of at least 10 Pa·s, more preferred at least 50 Pa·s, and most preferred at least 100 Pa·s (measured at a shear rate of 0.1 s⁻¹). Preferably, the viscosity is increased from a level of about 1-50 Pa·s at a shear rate of 0.1 s⁻¹ before entering the pre-reactor, to a level of about 50-500 Pa·s at a shear rate of 0.1 s⁻¹ after leaving the pre-reactor. The viscosity can be measured by standard rheometers, such as plate-and-plate rheometers, cone-and-plate rheometers or bob-and-cup rheometers.

[0012] (VBT: I have amended the viscosity ranges, because the viscosities used in the examples were outside the ranges mentioned her . Further I hav created a fallback position for a viscosity change, to overcome any clarity objections vis-a-vis the overlapping range of the initial viscosity and the viscosity after destabilisation).

If desired, the viscosity inside the pre-reactor can be controlled to manageable levels by using high shear mixing or ultrasound treatment. The pre-reactor can also have the form of a slurry mill or grinder.

[0013] The pre-reactor preferably has a controlled residence time. The residence time can vary depending on the exact configuration of the pre-reactor, but typically ranges from 1 to 180 seconds, and preferably from 30 to 90 seconds.

[0014] Destabilisation of the catalyst precursor mixture is performed in the pre-reactor just before shaping. The time period involved, i.e. the time elapsing between the start of the destabilisation and the shaping, depends on the exact configuration of the pre-reactor and on the time needed thereafter for the destabilised mixture to reach the shaping apparatus. Time periods of up to half an hour are possible, but may be less preferred for economical reasons. Preferred is a time period of less than 300 seconds. A more preferred time period is less than 180 seconds.

[0015] The catalyst precursor mixture can be destabilised for instance by temperature increase, pH increase or pH decrease and addition of gel-inducing agents such as salts, phosphates, sulphates, (partially) gelled silica (See: C.J. Brinker, G.W. Scherer, *Sol Gel Science*, Academic Press, 1990). The pH can be changed by addition of a pH regulating agents (acids and/or bases, such as HNO_3 , HCl , NaOH , NH_4OH etc.)

[0016] Catalyst components or precursors thereof can be fed to the pre-reactor from one or more holding vessels. Suitable catalyst components include zeolites (e.g. Y-zeolites, including H-Y-zeolites and USY-zeolites, zeolite beta, MCM-22, and MCM-36, ZSM-5, as are described in *ATLAS OF ZEOLITE STRUCTURE TYPES*, W.M. Meier and D. H. Olson, 3rd revised edition (1992), Butterworth-Heinemann, clays (e.g. kaolin, treated kaolin, bentonites, (doped) anionic clays such as hydrotalcite and doped hydrotalcite, smectites), alumina (Al_2O_3 , aluminium trihydrate and its thermally treated forms, boehmite) and binder materials (e.g. silica sol, waterglass, peptised alumina, aluminium chlorohydrol or mixtures thereof). In one embodiment of this invention all or a portion of the binder material precursor can be fed to the pre-reactor as pH regulating agent. Especially phosphate activated zeolites, (doped) anionic clays such as hydrotalcite and doped hydrotalcite are suitable pH regulating agents.

[0017] Aluminium chlorohydrol typically possesses the formula $\text{Al}_{2+m}(\text{OH})_{3m}\text{Cl}_6$ wherein m has a value of about 4 to 12. Aluminium chlorohydrol solutions are also frequently referred to in the art as polymeric cationic hydroxy aluminium complexes or aluminium chlorohydroxides which are polymers formed from a monomeric precursor having the general formula $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$. The preparation of an aluminium chlorohydrol solution is typically disclosed in US 2,196,016, CA 967,136 and US 4,176,090. Typically, preparation of aluminium chlorohydrol involves reacting aluminium metal and hydrochloric acid in amounts which will produce a composition having the formula indicated above. Furthermore, the aluminium chlorohydrol may be obtained using various sources of aluminium such as alumina (Al_2O_3), boehmite or aluminium trihydrate or its thermally treated form, (treated) clay and/or mixtures of alumina and/or clay with aluminium metal. Preferably, the aqueous aluminium chlorohydrol solutions used in the practice of the present invention will have a solids content ranging from about 15 to 50 percent by weight Al_2O_3 . Preferably 30-40 percent weight. Also aluminium chlorohydrol-containing compositions can be fed to the pre-reactor as a binder material. Such a composition may suitably be prepared by reaction of aluminium trihydrate, its thermally treated form or boehmite with HCl . Analogous nitric based alumina sols may be prepared by reaction of the above-mentioned alumina sources and nitric acid.

[0018] As said above, the catalyst precursor mixture can be destabilised by either a temperature change or by a change in pH. The desired pH or temperature will depend on the gelling or polymerisation properties of the binder used and the rest of the catalyst composition. This pH generally ranges from about 1 to 6.5. The desired temperature generally ranges from about 15° to 35°C, typically ambient. Aluminium chlorohydrol-containing mixtures will typically be destabilised by increasing the temperature to about 40°-99° or by changing the initial pH of the mixture from about 4.0 to below about 3.5 or from 4.0 to higher than about 4.5; Silica sol, waterglass- and peptised alumina-containing mixtures are typically destabilised by increasing the temperature to about 40°-99°C. Waterglass- and/or silica sol-containing mixtures may also be destabilised by increasing the initial pH, which is in the range of 1 to 5 and typically between 2.5 and 3.5, to a destabilisation pH in the range 3-10, typically between 4 and 6. As mentioned above, silica sol may be sodium free or not. Peptised alumina-containing mixtures may also be destabilised by increasing the initial pH which is in the range of 3 to 5 to a destabilisation pH of 4 or higher. It should be noted that the initial pH and the destabilisation pH of the mixture depend on the total composition of the mixture and therefore, the optimal pH for destabilisation should be determined for specific mixtures.

The optimal pH for destabilisation can easily be determined by preparing a catalyst composition consisting of the various components and to vary the pH using for instance an acid like HCl or HNO_3 and establishing the viscosity after a certain time as function of pH. The same can be done using a base like NH_4OH to vary the pH. It is important to verify that prior to destabilisation, peptisable compounds when present are well peptised. This will result in the best combination of accessibility and catalyst strength after destabilisation. Temperatures are measured by thermocouples. The pH of the mixtures is measured by usual pH probes.

[0019] The temperature of the pre-reactor is typically controlled by external heating means, whereas the pH is con-

trolled by adding a pH regulating agent. This agent can be either acidic or a basic, depending on the pH of the catalyst precursor mixture. Thus, destabilisation can be promoted by addition of an acid or base stream.

[0020] Suitable pH regulating agents include slurries or solutions of sodium hydroxide, ammonium hydroxide, nitric acid, sodium aluminate, magnesium oxide, sodium silicate, silica sol, sodium-free silica, sodium phosphate, ammonium phosphate, and diammonium phosphate. The pH regulating agents mentioned above also have a viscosity reducing effect. The use of said pH regulating agents also allows working with high solid slurries with a solid content between 35 and 50 wt%. Further, it is possible to first use a pH regulating agent to reduce the viscosity and subsequently use another pH regulating agent for destabilisation. Which agent will be used depends on the application of the resulting catalyst.

For instance, upon using sodium aluminate, interaction of the aluminium ions with silica present in the catalyst will introduce additional acid sites, whereas the addition of sodium silicate can promote silica sol formation, which can provide extra binding properties. Silica sol as such, for example in its ammonium stabilised form, is also a very suitable pH regulating agent. As mentioned above also phosphate activated zeolites, anionic clays such as hydrotalcite and doped hydrotalcite can suitably be used as pH regulating agents.

[0021] Magnesium oxide, or MgO containing components as for instance hydrotalcite, can in addition introduce vanadium passivation capacity and SOx reduction capabilities to the catalyst, while phosphates (as for instance Sodium phosphate, ammonium phosphate and/or phosphoric acid) in addition promotes passivation of the zeolite non-framework alumina or of other amorphous alumina species in the catalyst.

[0022] Phosphates can also be added to activate and/or stabilise the zeolites like for instance in the case of phosphate activated ZSM-5. Also a pre-treated stream of these phosphate activated zeolites can be added in this pre-reactor to simultaneously function as a pH regulating agent, while avoiding the loss of activation which might occur if the pH is not adjusted.

[0023] Additives can be added to the catalyst precursor mixture in the pre-reactor or to the pH regulating agent. Suitable additives comprise compounds of rare earth metals (for example Ce, La), Si, P, B, group VI, group VIII, alkaline earth (for instance Ca, Mg or Ba) and/or transition metals (for example W, V, Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn). Suitable sources of these compounds are oxides, hydroxides, acetates, oxalates, carbonates, nitrates, and halides. Preferred additives are rare earth metals, magnesium compounds, alumina, Na_3PO_4 and $(\text{NH}_4)_3\text{PO}_4$.

[0024] After destabilisation the catalyst is shaped. Suitable shaping methods include spray-drying, pelletising, extrusion (optionally combined with kneading), beading, or any other conventional shaping method used in the catalyst and absorbent fields or combinations thereof. A preferred shaping method is spray-drying.

[0025] The process of the present invention can be used for the preparation of various catalysts and catalyst additives, such as fluid catalytic cracking catalysts, fluid catalytic cracking additives as SOx reduction, NOx reduction, CO combustion additives, ZSM-5 additives, sulfur in gasoline reduction additives, hydroprocessing catalysts, alkylation catalysts, reforming catalysts, gas-to-liquid conversion catalysts, coal conversion catalysts, Hydrogen manufacturing catalysts, and automotive catalysts.

[0026] The invention is illustrated by the following examples.

EXAMPLES

[0027] The accessibility of the catalysts prepared according to the Examples below was measured by adding 1 gram of the catalyst to a stirred vessel containing 50 g of a 15 g/l Kuwait vacuum gas oil (KVGO) in toluene solution. The solution was circulated between the vessel and a spectrophotometer, whereby the KVGO-concentration was continuously measured.

The accessibility of the catalysts for KVGO was quantified by the Akzo Accessibility Index (AAI). The relative concentration of KVGO in the solution was plotted against the square root of time. The AAI is defined as the initial slope of this graph:

$$\text{AAI} = -d(C_t/C_0)/d(t^{1/2}) \cdot 100\%$$

[0028] In this equation, t is the time (in minutes) and C_0 and C_t denote the concentrations of high molecular weight compound in the solvent at the start of the experiment and at time t , respectively.

[0029] The attrition resistance of the catalysts was measured by the both a standard Attrition Test and the so-called Hot Attrition Test. Both these tests are based on the usual air jet apparatus as pioneered by Forsythe and Hertwig (Ind. Eng. Chem., vol. 41, 1977, pp.1200-1206).

[0030] The Hot Attrition Test is carried out at high temperatures (700°C) for it to be realistic for gauging fines generation in FCC regenerators.

In this test the catalyst bed resides on an attrition plate with three nozzles. The attrition plate is within an attrition tube

which is heated at 700°C by way of radiate heat. Air is forced to the nozzles and the resulting jets bring about upward transport of catalyst particles and generated fines. On top of the attrition tube is a separation chamber where the flow dissipates and most particles larger than about 16 microns fall back into the attrition tube. Smaller particles are collected in a collection bag.

[0031] The Hot Attrition Index (HAT) is reported as the weight percentage of fines collected in the collection bag after 24 hours, based on a fictive intake of 50 grams. So, more attrition resistant catalysts will result in lower HAT values.

[0032] The standard Attrition Test is comparable to the Hot Attrition Test, except for the temperature, which is ambient in the standard test. After calcination of the samples at 600°C, the test is first run for 5 hours to measure the initial (0 - 5 hours) attrition and then for another 15 hours to get the inherent (5 - 20 hours) attrition. The Attrition Index (AI) is the extrapolated % attrition after 25 hours.

[0033] It is our experience that the Hot Attrition Test is a better measure for the simulation of Industrial FCC attrition and hence a better indicator for commercial catalyst losses and emissions than the standard attrition test

Comparative Example 1

[0034] A catalyst precursor mixture with a total solids content of 25% comprising 24 parts by weight (pbw) RE-USY, 8 pbw boehmite alumina (Condea Pural 200®), 8 pbw aluminium chlorohydrate, 40 pbw kaolin and 25 pbw water was prepared by adding water to the holding vessel, followed by zeolite, boehmite, aluminium chlorohydrate and kaolin.

[0035] The slurry was fed to a pre-reactor with a volume of 1 litre with a residence time of 25 seconds. The slurry was homogenised in the pre-reactor by way of high shear mixing using an EKATO-INTERMIG® impeller at 1800 rpm. Spray-drying was performed with an inlet temperature of 400°C and an outlet temperature of 120°C. The pH of the catalyst precursor mixture was 4.3; the temperature was 25°C; and the viscosity was 5 Pa·s at a shear rate of 0.1 s⁻¹. The viscosity was measured using a Physica® UDS rheometer with a cone-and-plate configuration. In this Comparative Example the mixture was not destabilised before spray-drying.

[0036] The Akzo Accessibility Index (AAI) of this comparative catalyst A was 8.5. The Attrition Index (AI) of this catalyst was 10.2; The Hot Attrition Index (HAT) was 8.5.

Example 2

[0037] Catalysts B-F were prepared in the same way as comparative catalyst A of Comparative Example 1, the difference being that 1 minute before spray-drying the mixture was destabilised by the continuous addition (residence time: 25 seconds) of either a 10 wt% HCl solution (Catalysts B and C), a 10 wt% NaOH solution (Catalysts D and E) or a 10 wt% NH₄OH solution (Catalyst F) to the pre-reactor. After destabilisation the viscosity had increased to 75 Pa·s at a shear rate of 0.1 s⁻¹.

The pH of the mixtures after this destabilisation is presented in Table 1, together with the resulting Akzo Accessibility Index (AAI) and the Hot Attrition Index (HAT).

Table 1

Catalyst	Comparative catalyst A	B	C	D	E	F
Acid/base	-	HCl	HCl	NaOH	NaOH	NH ₄ OH
Final pH	4.3	3.0	2.0	5.2	6.1	5.6
AAI	8.5	8.8	9.3	8.9	9.2	9.7
HAT	8.5		6.5		9.8	12.4
AI	10.2	7.5	10.1	9.8	20.4	20.2

[0038] These results show that with the method according to the invention catalysts with improved accessibility were obtained as compared to catalysts obtained under like conditions without destabilisation. Moreover the invention offers a way to prepare catalysts which possess both higher accessibility and better attrition resistance compared to conventionally prepared catalysts.

Comparative Example 3

[0039] A catalyst precursor mixture with a total solids content of 30% comprising 23 parts by weight (pbw) RE-USY, 10 pbw boehmite alumina (CP 1.5®, ex Alcoa), 10 pbw aluminium chlorohydrate, 2 pbw of a sodium free silica sol, 35 pbw kaolin and 20 pbw water was prepared by adding water to the holding vessel, followed by zeolite, boehmite, aluminium chlorohydrate and kaolin.

[0040] The slurry was fed to a pre-reactor with a volume of 1 litre with a residence time of 25 seconds. The slurry was homogenised in the pre-reactor by way of high shear mixing using an EKATO-INTERMIG® impeller at 1800 rpm. Spray-drying was performed with an inlet temperature of 400°C and an outlet temperature of 120°C. The pH of the catalyst precursor mixture was adjusted to 3.0; the temperature was 25°C; and the viscosity was 5 Pa·s at a shear rate of 0.1 s⁻¹. The viscosity is measured using a Physica® UDS rheometer with a cone-and-plate configuration. In this Comparative Example the mixture is not destabilised before spray-drying.

The catalyst was calcined to harden and remove the chlorides

[0041] The Akzo Accessibility Index (AAI) of this comparative catalyst G was 5.8. The Attrition Index (AI) of this catalyst was 4.1; The Hot Attrition Index (HAT) was 8.2.

Example 4

[0042] Catalysts H-L were prepared in the same way as the catalyst of Comparative Example G, the difference being that 1 minute before spray-drying the mixture was destabilised by the continuous addition (residence time: 25 seconds) of either a 10 wt% NaOH solution or a 10 wt% NH₄OH solution to the pre-reactor. After destabilisation the viscosity had increased to 75 Pa·s at a shear rate of 0.1 s⁻¹.

[0043] The pH of the mixtures after this destabilisation is presented in Table 1, together with the resulting Akzo Accessibility Index (AAI) and the Hot Attrition Index (HAT).

Table 2

Catalyst	Comparative catalyst G	H	I	J	K	L
Acid/base	-	NaOH	NaOH	NH ₄ OH	NH ₄ OH	NH ₄ OH
Final pH	3.0	3.9	4.3	3.5	4.1	5.0
AAI	5.8	9.7	11.8	8.6	14.4	20.2
HAT	8.2		8.4	8.2	8.6	18.8
AI	4.1	7.5	12.7	6.1	17.2	25.7

[0044] These results show again that with the method according to the invention catalysts with improved accessibility were obtained as compared to catalysts obtained under like conditions without destabilisation, while maintaining good Hot Attrition values. The invention offers a way to prepare catalysts which possess very high accessibility and still reasonable strength.

Claims

1. Process for preparing a catalyst comprising combining catalyst components or precursors thereof in an aqueous medium to form a catalyst precursor mixture, feeding the mixture to a shaping apparatus and shaping the mixture to form particles, **characterised in that** just before the shaping step the mixture is destabilised.
2. Process according to claim 1, **characterised in that** the mixture is destabilised less than 300 seconds before the shaping step.
3. Process according to claim 1 or 2, **characterised in that** shaping is performed by spray-drying, extrusion, pelletising or beading.
4. Process according to any one of the previous claims, **characterised in that** the catalyst is an FCC catalyst.
5. Process according to claim 4, **characterised in that** the shaping is performed by spray-drying.
6. Process according to any one of the previous claims, **characterised in that** the catalyst precursor mixture comprises aluminium chlorohydrate or an aluminium chlorohydrate-containing composition.
7. Process according to claim 6, **characterised in that** the aluminium chlorohydrate-containing composition has been produced by (partially) reacting aluminium trihydrate (boehmite) or its thermally treated form with HCl.

8. Process according to claim 6 or 7, **characterised in that** the catalyst precursor mixture comprises a nitric based alumina sol.
9. Process according to claim 8 wherein the nitric based alumina sol has been produced by (partially) reacting aluminium trihydrate (boehmite) or its thermally treated form with HNO_3 .
10. Process according to any one of the preceding claims wherein an acid or base stream is added to promote destabilisation.
11. Process according to any one of claims 6-10, **characterised in that** destabilisation is performed by decreasing the pH from 4 to below 3.5 or increasing the pH from 4 to above 4.5.
12. Process according to any one of the claims 1-10, **characterised in that** the catalyst precursor mixture comprises waterglass and/or a silica sol which is sodium free or not.
13. Process according to claim 12, **characterised in that** destabilisation is performed by increasing the initial pH which is in the range of 1 to 5 to a destabilisation pH in the range of 3-10.
14. Process according to claim 13, **characterised in that** destabilisation is performed by increasing the pH from 2.5-3.5 to a pH between 4-6.
15. Process according to any one of the claims 1-10 and 12, **characterised in that** the catalyst precursor mixture comprises peptised alumina.
16. Process according to claim 15, **characterised in that** destabilisation is performed by decreasing the initial pH which is in the range of 3 to 5 to a destabilisation pH of 4 or higher.
17. Process according to any one of the claims 1-10, 12 or 15, **characterised in that** destabilisation is performed by changing the temperature from 15-35 °C to 40-99°C.
18. Process according to any one of the claims 1-16, **characterised in that** the pH is changed by addition of a pH regulating agent.
19. Process according to claim 18 wherein the pH regulating agent is sodium hydroxide, ammonium hydroxide, nitric acid, sodium aluminate, magnesium oxide, sodium silicate, silica sol, sodium phosphate, ammonium phosphate and/or diammonium phosphate.
20. Process according to claim 18 wherein the pH regulating agent is a phosphate treated zeolite, and/or a mixture of phosphate and zeolite, anionic clay and/or anionic clay and/or doped anionic clay.
21. Process according to claim 20 wherein the pH regulating agent is anionic clay or doped anionic clay, said anionic clay being stabilised by hydrothermal treatment or being prepared under hydrothermal conditions.
22. Catalyst obtainable by the process according to any one of the previous claims.
23. Catalyst **characterised in that** it has an Akzo Accessibility Index higher than 10 and a Hot Attrition Index lower than 15.
24. Catalyst according to claim 23, comprising a phosphate treated zeolite, or a mixture of phosphate and zeolite.
25. Catalyst according to claim 23 or 24, comprising an anionic clay or doped anionic clay.
26. Catalyst according to claim 25, wherein the anionic clay is a hydrotalcite or hydrotalcite-like material or a doped version thereof.
27. Catalyst according to claim 25 or 26 wherein the anionic clay or doped anionic clay has been stabilised by hydrothermal treatment or preparation under hydrothermal conditions.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 2146

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 October 2001	Examiner Thion, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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